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THE SYNTHESIS OF SUBSTITUTED NICKEL DITHIENE COMPLEXES WITH INT--ETC(U)  
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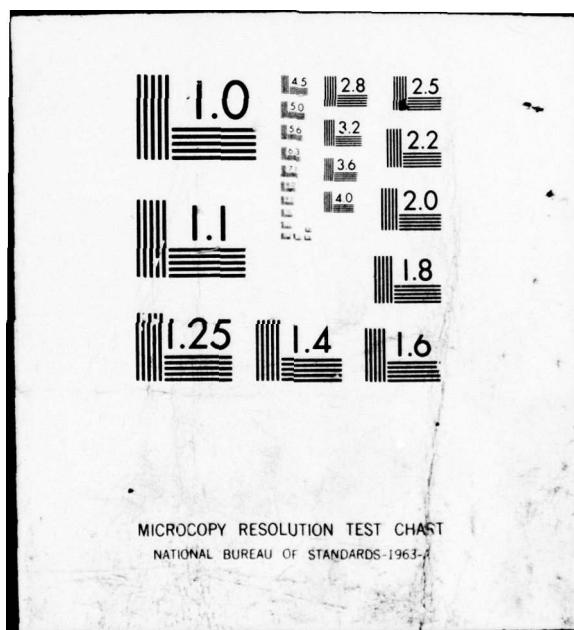
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THE SYNTHESIS OF SUBSTITUTED NICKEL DITHIENE COMPLEXES  
WITH INTENSE ELECTRONIC TRANSITIONS IN THE INFRARED REGION

A. Nazzal, R. W. Lane, J. J. Mayerle and U. T. Mueller-Westerhoff

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SUMMARY

In attempting to determine the factors which allow the intense IR absorption of dithiene complexes to be shifted towards the  $2\mu$  range, we have synthesized a number of new nickel complexes of the dithiene type.

Rigidity and coplanarity of the ligands were found to be indispensable. The effect of electron donating substituents on the long-wavelength transition was found to be in accordance with the predictions based on previous work in our laboratory. This effect was maximized by incorporation of the substituents into rigid ring systems.

With strong donors directly attached to the dithiene complex rings, the electron donor properties of the complex become so strong that the neutral species are unstable: two electron oxidation leads to the dications, which no longer posses an IR absorption.

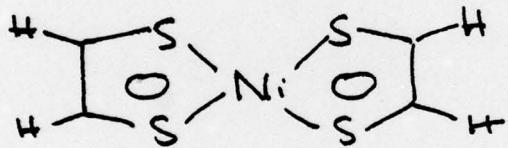
The longest wavelength absorption obtained in this work lies at  $1.37\mu$ .

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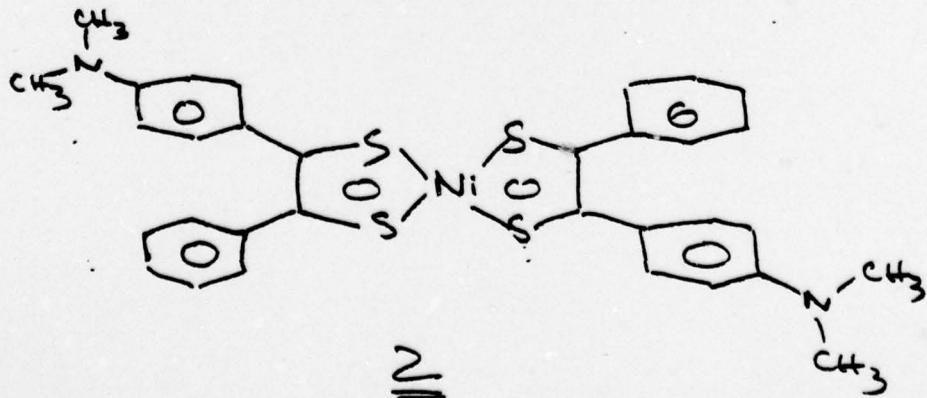
## INTRODUCTION

The development of lasers operating in the infrared region between 1.0 and  $2.0\mu$  has brought with it the need for passive Q-switch materials which absorb strongly in this region and which are thermally and photochemically stable.

Dithiene complexes (formula 1, often also called dithiolene complexes) are excellent candidates for the synthesis of materials with such properties. They show intense electronic transitions in the near infrared which, by appropriate substitution, can be shifted to very low energies.

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One substituted dithiene complex, compound 2, with  $\lambda_{max}$  at  $1.06\mu$ , has been shown to effectively Q-switch the Nd glass laser and to be so stable that it can even be used for this purpose in a solid polymer matrix.



In our approach to synthesize new dithienes with intense absorptions at wavelengths above  $1.06\mu$  we were guided by two main considerations. Firstly, it was clear from our previous work that electron donating substituents have the desired effect. It was thus one aim to provide amino-type substituents in the proper positions of the dithiene and to determine their effect upon position and intensity of the resulting electronic transitions. Secondly, to maximize the effect of the substituents their  $\pi$ -molecular orbitals have to utilize the best possible overlap with the dithiene ring system, i.e. they should be coplanar. In 2 and all other phenyl-substituted dithienes it is not possible for all rings to be coplanar, since the  $\alpha$ -hydrogens in this cis-stilbene type system are in each others way. The known structure of the tetraphenyl-dithiene nickel complex shows the expected out-of-plane twist. This work therefore, concentrated on the synthesis of complexes in which both the aromatic rings and their substituents were forced into complete coplanarity with the dithiene. In addition, we also investigated two types of complexes, in which the electron donating groups were directly attached to the dithiene ring, without an intervening aromatic ring. In such a structure, the full effect of the substituent on the position of the electronic transition would be felt. However, quantum mechanical calculations (carried out in cooperation with Prof. G. Loew at Stanford and her students) on systems of this type pointed out a problem in this approach, which we will briefly describe here.

The square planar dithienes of the Ni, Pd and Pt series possess a very low lying empty molecular orbital (Fig. 1a). The electronic transition

HOMO  $\rightarrow$  LUMO is the observed intense (allowed) absorption in the infrared. Shifting the relative energies of HOMO and LUMO such that  $\Delta E$  becomes smaller is the key to obtaining complexes with absorptions at lower energy. Substituting the parent dithiene ring system with electron withdrawing groups (Fig. 1b) leads to a stabilization of both HOMO and LUMO by about the same amount. As a result, the electronic transition is not appreciably shifted. Adding electron donating substituents destabilizes the HOMO more than the LUMO. Therefore, the gap is decreased and a shift of this transition to longer wavelengths is to be expected. (Fig. 1c). However, very strong donors, which would produce the most drastic shifts, destabilize the HOMO so much that it becomes antibonding. (Fig. 1d). The system, therefore, will tend to give up the two electrons in the HOMO and prefers to exist as a dication, which then no longer will show the desired low energy transition.

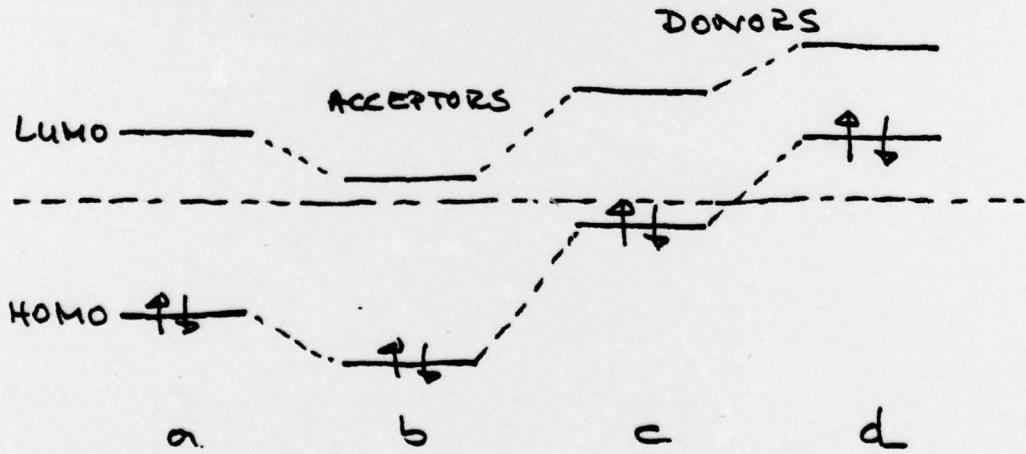


Figure 1: Frontier Orbitals in Dithiene Complexes (HOMO = highest occupied molecular orbital; LUMO = lowest unoccupied molecular orbital. Energies are relative. For explanations see text.)

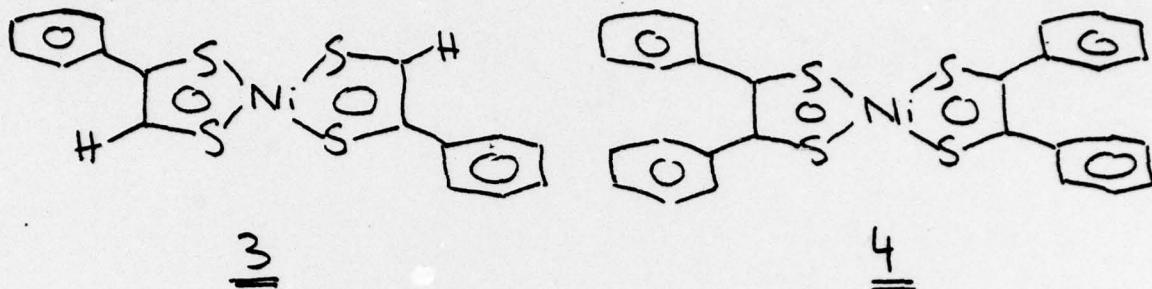
While in purely organic dyes (as for instance cyanines) the photochemical instability sets a limit to shifting the  $\pi\rightarrow\pi^*$  transition to wavelengths longer than  $1\mu$ , the dithienes appear to suffer from the limitation of being too easily oxidized to allow the synthesis of materials with absorptions at very low energies.

In the present work, we have attempted to investigate these limitations and to experimentally determine the factors which would lead to shifts in the desired direction.

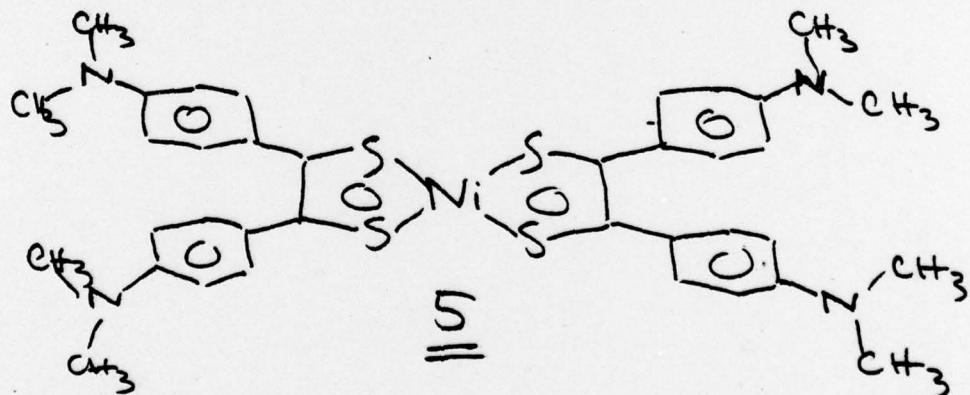
#### RESULTS AND DISCUSSION

For reasons of uniformity, we have investigated only the nickel complexes as representatives of the series of  $d^8$  square planar dithienes. This was done in spite of the fact that in the series Ni, Pd, Pt, the Pd complexes show the longest wavelength absorption. Since the primary goal was to establish the influence of the different ligands, it was felt that the above limitation to nickel complexes was justified.

The parent compound 1  $\text{Ni}(\text{S}_2\text{C}_2\text{H}_2)_2$  absorbs at 720 nm. If one phenyl group is introduced into each half of the complex (compound 3) the  $\lambda_{\max}$  shifts to 803 nm. With two phenyl groups (compound 4)  $\lambda_{\max}$  lies at 866 nm. While the shift of the first phenyl group amounts to about 0.18 eV, the second one only adds another 0.11 eV, since here the problem of coplanarity arises.

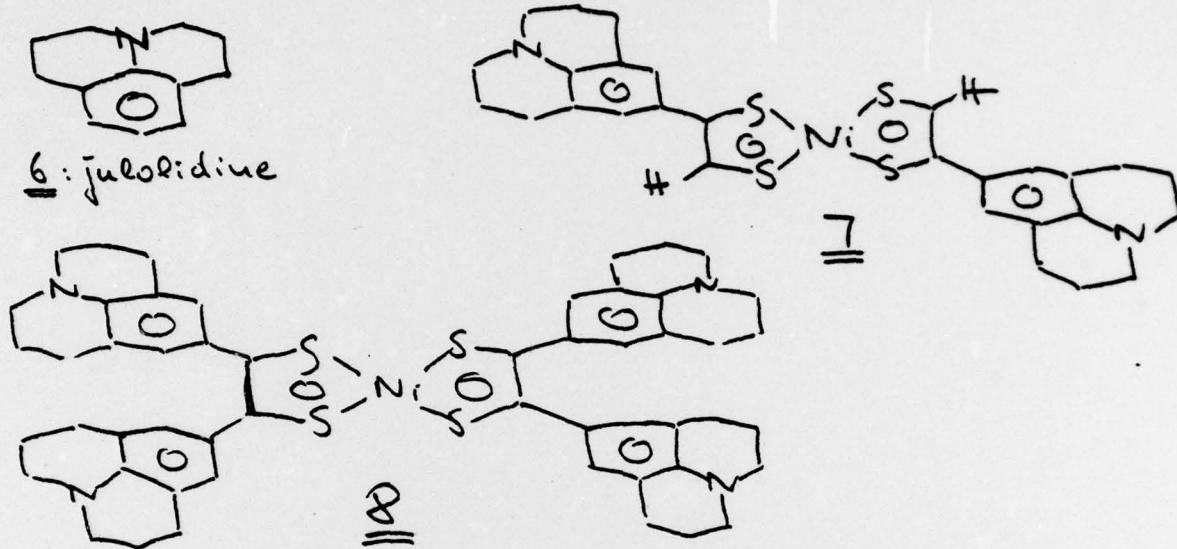


Comparing the tetraphenyl-dithiene nickel 4 to the Q-switch 2, in which one of the phenyl rings on each side carries a dimethylamino group, one observes the drastic shift of 0.26 eV. Here, it is probable but not proven that the substituted ring enjoys greater coplanarity than the unsubstituted one, because only in this way the conjugation can be maximized. A second dimethylamino group (complex 5) shifts the transition by only 0.07 eV further than in 2, because here all rings are equally twisted out of plane.



The most drastic illustration of the effect of coplanarity comes from the julolidine-substituted dithienes. Julolidine (6) is a dialkylamino-benzene in which the amino-substituent is held rigidly coplanar by incorporation into a saturated six-membered ring. Going from the parent dithiene 1 to

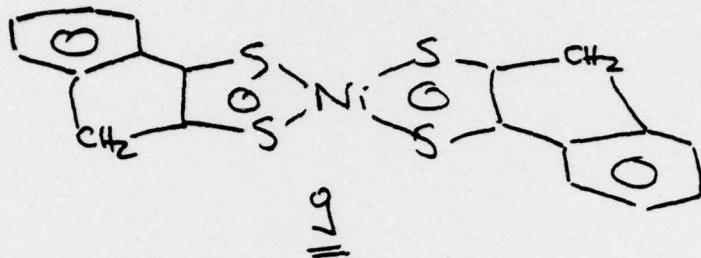
the mono-julolidine dithiene 7, an immense shift of 0.67 eV to 1180 nm is realized. The bis-julolidine-dithiene again suffers from coplanarity problems and absorbs only 0.07 eV further than compound 7.



It is also important to note the effect of the non-rotating amino substituent on the extinction coefficient: while the tetra-dimethylaminophenyl-dithiene nickel (5) has an extinction coefficient of about 28000, the julolidine complex 8 has  $\epsilon=45000$  at  $1.27\mu$ .

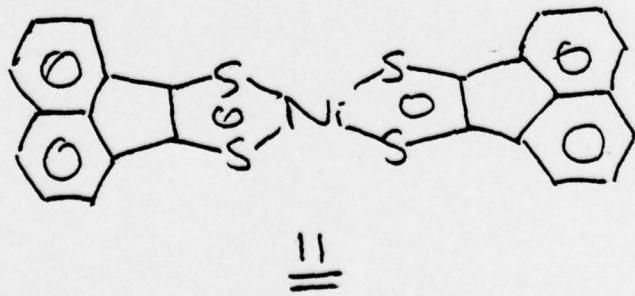
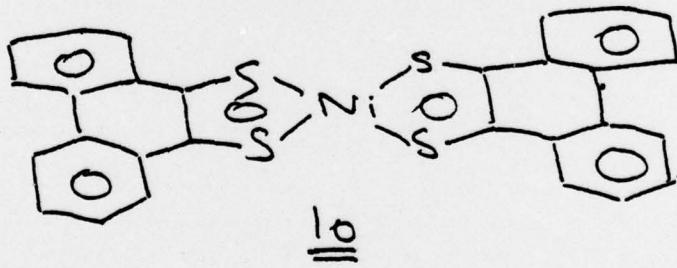
Having established these factors, it became necessary to establish the influence of the coplanarity of the phenyl-substituents themselves. It was noted earlier that going from 1 to the phenyl-substituted complex 3 led to a shift of 0.18 eV. It was therefore of interest to see which effect the fixing of this substituent into coplanarity would have on the position of the infrared transition. This was achieved by synthesizing complex 9, which shows  $\lambda_{\text{max}}$  of 915 nm. The difference of 0.19 eV between the absorptions of 9 and 3 is, however, not the true effect of coplanarity

alone, since the methylene bridge in 9 also produced a bathochromic shift. One can, however, approximate the planarity effect in the following way: the tetramethyl-dithiene nickel absorbs at 770 nm. The shift from the



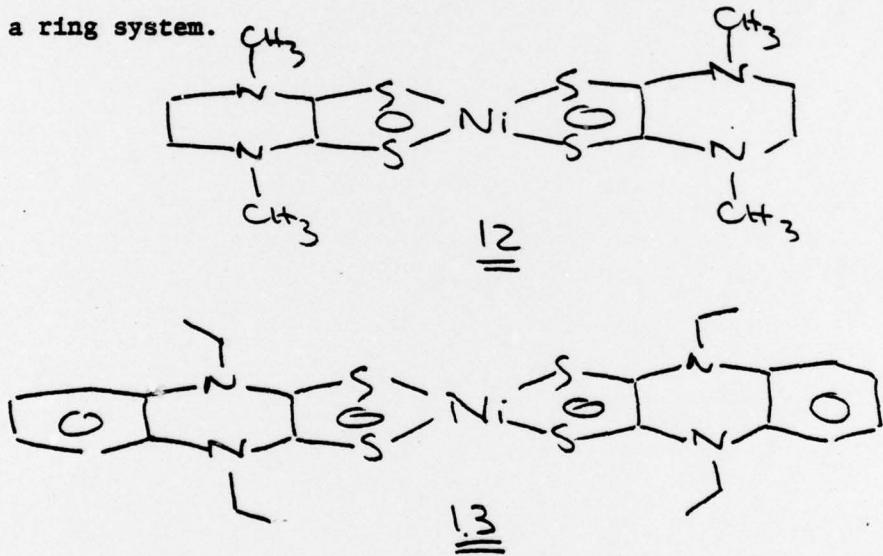
unsubstituted parent system is 0.12 eV, or 0.06 eV per methyl group.

Substracting this from the shift 3→9, one is left with about 0.13 eV for the planarity effect alone. A similar magnitude for the bathochromic shift due to complete coplanarity is observed in going from the tetraphenyl dithiene 4 to the phenanthrene-dithiene 10: this complex absorbs at 966 nm, 100 nm or 0.15 eV lower than the nonplanar 4.



A structurally related but independent system is the acenaphthene complex 11, which was prepared in a multistep synthesis similar to that of 10. The acenaphthene complex absorbs at  $1.14\mu$  and promises to be a system of great value, if proper substitution by electron donating groups can be achieved.

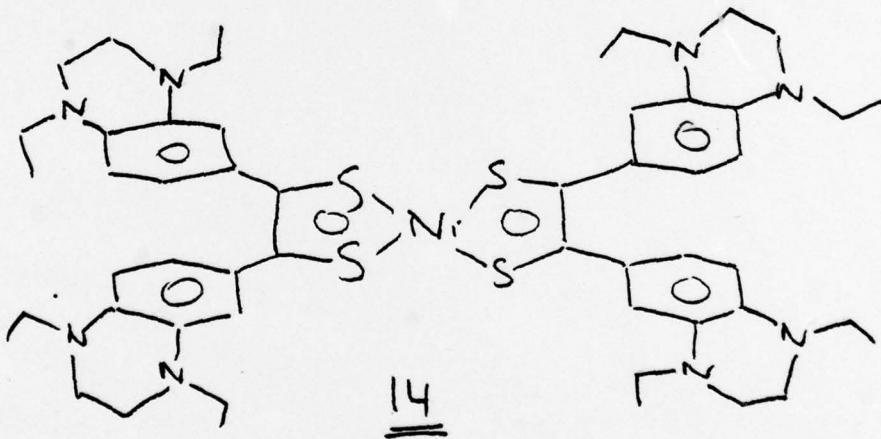
The attachment of electron donating groups directly to the dithene rings was achieved in two systems. In compounds 12 and 13 these substituents are furthermore forced into coplanarity with the complex by incorporation into a ring system.



Both complexes were quite a disappointment in that no infrared transitions could be detected in either one of them. In view of the fact that 12 and 13 are easily oxidized to their respective dications, no definite conclusions can be drawn from our failure to observe the expected infrared bands. This could simply be a consequence of not sufficiently rigorous experimental conditions in determining the spectral properties. There is

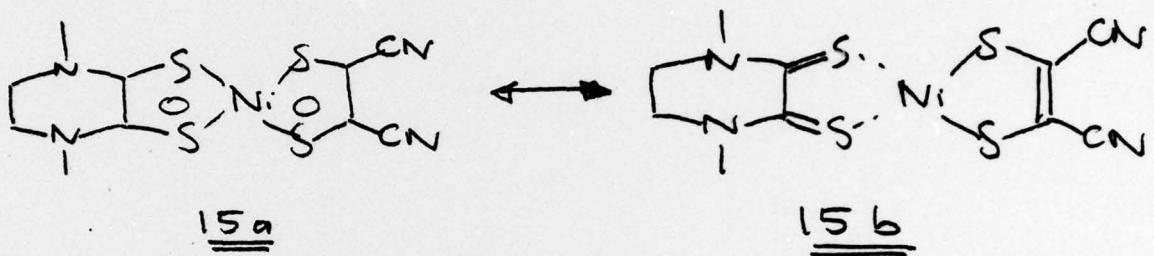
no general explanation at this time for the lack of a band in the region between  $1.5$  and  $2\mu$ .

The presence of two electron donating groups in each phenyl ring of a tetraphenyldithiene nickel was deemed to have additional bathochromic effect beyond that observed for the dimethylamino- or julolidine-derivatives. This was found to be true for compound 14, which carries amino-substituents in the para- and meta-positions of the phenyl ring. The substituents are fixed as in the julolidine case. This compound shows the lowest energy transition observed so far for any dithiene complex. The band at  $1.37\mu$  appears to be strong, but no exact determination of the extinction coefficient was made, since due to the poor solubility of 14 sufficient purification was not possible.



Finally, we have investigated one extreme example of push-pull substitution of the dithiene system. It is known from many organic compounds that the presence of electron-donating and - withdrawing substituents in one ring system has a strong bathochromic effect. In our case, compound 15, the

very strong electron donating dialkylamino-substituents are opposed by the strongly electron-withdrawing cyano groups. Complex 15 absorbs at 775 nm, indicating that in this case the polar structure has become too dominant. Complex 15 exists as a dithiolate coordinated to a dithio-oxamide (structure 15b). The dithiene resonance (structure 15a) and with it the low energy transition has been lost.



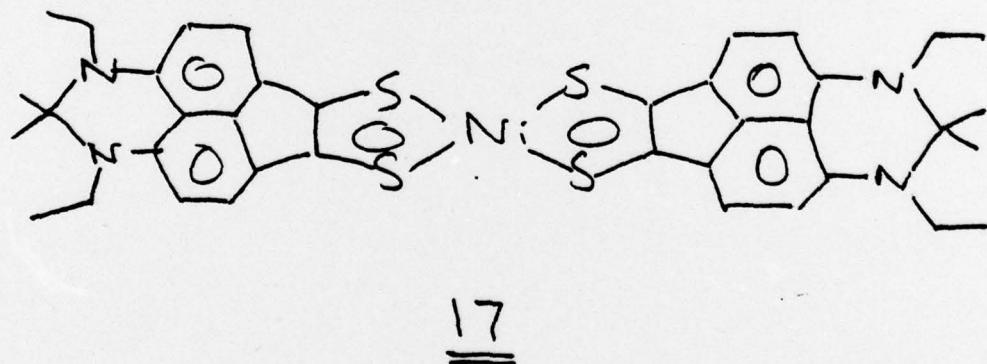
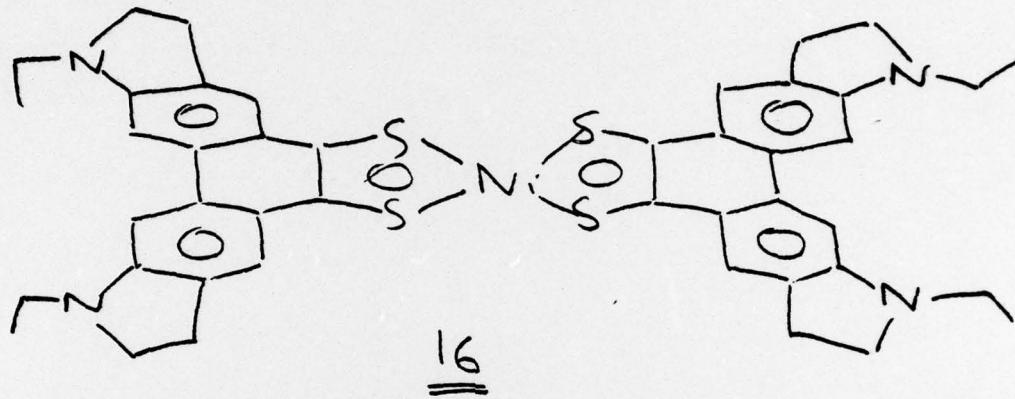
#### CONCLUSION

This work has established the requirements for the structure of ligands which allow the near-infrared transitions of dithiene complexes to be shifted towards longer wavelengths. It seems entirely possible that a material with an intense ( $\epsilon > 30000$ ) absorptions at  $2\mu$  can be made.

In two newly synthesized compounds, we have apparently overshot this goal and it seems now reasonable to confine the choice of ligand systems to

the group of amino-substituted benzenoid aromatic compounds. If this work is continued, the synthesis of the following two complexes will be the first goal:

1. a phenanthrene-9,10-dithiolato complex with two rigidly fixed amino-substituents (compound 16)



2. the acenaphthene dithiolato complex 17, in which the amino-substituents are again fixed into coplanarity.

Initial efforts to prepare 16 and 17 have been made, but their synthesis is not trivial, and considerably more time has to be spent on this project.

The influence of our most effective ligands on the IR transition in complexes with metals other than nickel has not been investigated. Clearly this is an important aspect, which merits to be studied.

FIRST ELECTRONIC TRANSITIONS OF NICKEL DITHIENE COMPLEXES  
(The Numbering of Complexes Refers to their Structures in the Text)

<u>Complex</u>	<u>max</u> (nm)	<u>E</u> (eV)
1	720	1.72
2	1060	1.17
3	803	1.54
4	866	1.43
5	1130	1.10
7	1180	1.05
8	1270	0.98
9	915	1.35
10	966	1.01
11	1140	1.09
12	?	
13	?	
14	1370	0.90
15	775	1.60